Microsyst Technol (2016) 22(4): 817–822
DOI 10.1007/s00542-015-2454-2

TECHNICAL PAPER

Nanogaps formation and characterization via chemical and oxidation methods

Th. S. Dhahi

Received: 12 January 2015 / Accepted: 30 January 2015

Abstract Different materials were used to optimize the desired nano-size with smooth process and faster fabrication. Gold, polysilicon and silicon were used to apply this report (experimental). SOI and Si wafers have used as a substrate and one chrome mask to build up the nanogap devices using size reduction technique. Two chrome masks have used to fabricate the proposed pattern. Electrical characterization was applied to setup the fabricated devices with different materials. Conductivity and resistivity were measured to characterize the nanogap structure with gold, polysilicon and silicon as electrodes. However, gold nanogap has recorded an increment in the conductivity, and the silicon nanogap structures have recorded an increment in the resistivity comparing with the other used materials.

1 Introduction

Nano size based device have proof their capabilities to be employed in various applications ranging from energy, optics, diagnostic etc., (Dilled et al. 2014; Kim et al. 2011). These nano-ordered materials have attracted much attention various research communities since the device have advantages of various degree including low power consumption, sensitivity, selectivity, small size can be fit and operate in different forms and configuration due trend of density can be integrated to portable devices operate in In-situ (Kim et al. 2011). In addition, the device have shown potential properties which cannot be achieved by micro or bulk materials (Dhahi et al. 2011a, b). The Nano devices can be fabricated using two major approaches; top down and bottom up, these further divided into a variety of techniques for nano structures (Dhahi et al. 2011; Du et al. 2011; Zanetti et al. 2012). The bottom-up approach for the fabrication of nanostructure is the manipulation with atoms or molecules arrangement meaning by rearranging atom to bring in close proximity to form the desired structures. The elementary blocks is atom and is usually manipulated by physical arrangement or chemical reaction, sometime template can be employed to achieve a desired shape. However, through this approach achieving maintaining controlled chemical reactions for specific desired shape is very difficult. Therefore the best choice to employed for nanogap is top down. With the top-down technique, a wide variety of devices geometry can be manipulated with high reliability and high integrity. The approach is common in the semiconductor device fabrication, it has some limitation used using metals Du et al. (2010). How with careful design and process optimization, novel structure can be form. Nanogap fabricated with this approach is suitable for many applications and will soon take over the current practice especially on medical becasues the current diagnotic practices are quite costly, time consumming, complicated and required expert to interprete the results (Jemmy et al. 2011; Kanwar et al. 2011; Kim et al. 2012; Mampallil et al. 2014). Therefore, the development of technology that is specific and reliable for detecting dieases at early stages and easily accessible for functioning as the first-line guidance is of critical importance (Zhong et al. 2010; Hashim et al. 2010). The gap can be fabricated in such a way that can accommodated only single molecule and single-molecule measurements can provide information that is not achievable with traditional measurements system.

T. S. Dhahi (✉)
Department of Physics, College of Education for Pure Science, Basra University, Basra, Iraq
e-mail: sthikra@yahoo.com

T. S. Dhahi
Institute of Nanoelectronic Engineering, University Malaysia Perlis, Perlis, Malaysia

Published online: 11 February 2015

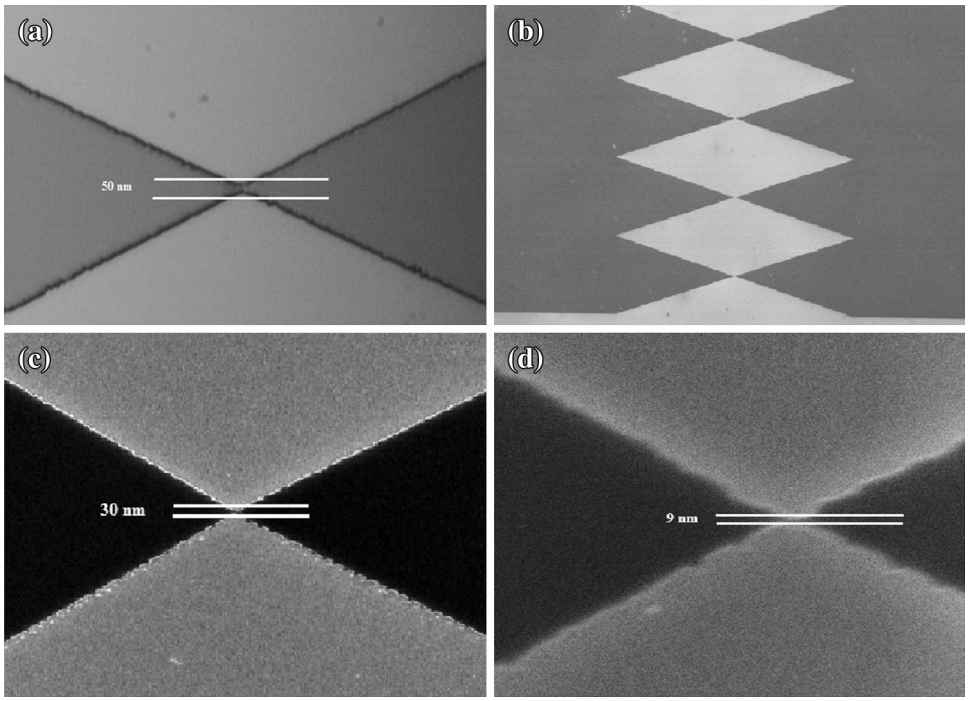

Fig. 1 FESEM images show gold electrode pattern after using an aqua regia solution (HCl 1:3 HN_3) sequent to remove undesired gold material between the two electrodes

Using nanodevices has been developing rapidly during the past few years and with this, properties of nanomaterials are being extensively studied and many attempts are made to fabricate appropriate nanodevice Du et al. (2010). However, many fundamental issue remain unsolved. Due to their unique optical, magnetic, mechanical, chemical and physical properties, nano materials a greater effort is needed to explore their potential. The current research present simple for fabrication and characterization method for producing gold, polysilicon and silicon nanogaps.

2 Materials and methods

The electrode design was performed by using AUTOCAD and transferred chrome marks, This followed by Fabrication process of the nanogap, it were realized by using 300 nm oxide deposited silicon substrate. After two steps (R2 & R1) of cleaning the substrate using HS-3624 ultrasonic machine, EZP520-87 resist is diluted in anisole is spin coated at speed (500 rpm) and 200 nm thickness was resist obtained after baked at 100 ℃ for 1 min. The electrode pad and gap line are then patterned using reactive ion etcher. In the electrodes electrical measurements, we used two electrodes separating them by a gap distance for three materials namely: gold, silicon and poly-silicon. This gap distances were experimentally found to be between 3 and 15 nm for gold materials, 6 and 86 nm for silicon and polysilicon to be 5 and 7 nm. These achieved sizes comparable to the size of the nucleotide molecules that can readily be employed to bio-molecular detection. The gap sizes were all reproducible and following method were employed photo-lithographically fabricated gold, silicon and poly–silicon nanogap on a thin oxide-deposited silicon substrate, a field emission scanning electron microscope (FESEM) image of typical fabricated nanogaps are shown in Fig. 1. The reproducible fabrication procedures for the lithographically defined gap electrode are described in detail in our previous publication (Dhahi et al. 2011, 2012).

3 Results and discussion

The nanogap is and two electrodes separated by a distance were behave much pretty like super capacitor, this has equally claimed by Ionescu et al. (2006). The device form conductive connection between the two electrodes separated by a non-conductive region. The non-conductive substance is called the dielectric medium. Since the device consist of the same material, theoretically super capacitors have no true polarity, due to this no abnormality behavior is expected. Figure 1 shows the typical nanogap fabricated using the above materials. The figure show the measurement three gaps sizes for gold materials 3, 5 and 15 nm with resistivity dropping from 14 to <1 nΩ, it is interesting to note the variation of the resistivity with gap sizes, 3 nm gap at 6 nΩ. Such a behavior would make these the nanogap useful in where selective detection of bio or electrical is necessary and in which a lower energy form for the operation activity needs to be employed. The small the gap,

it will response to short wave meaning device stability can sustain with high frequency and the ability to operate in short wavelengths range by decreasing the gap size is break through, the researchers are anticipating.

Unless the silicon and poly–silicon can easily etch with buffered oxide etcher (BOE), Au gold formation highly challenging because the resist need to etch lower than micro domain so as to etch the gold using aqua regia, in addition to this challenges it bigger grain size compared to other semiconductor family. However, with care design and systemic resist trimming and etching, it was possible to fabricate the required nanogap size and to produce more controllable and smaller dimensions of Au nano-gap electrodes, a hard mask is necessary and in this case aluminium is a good material for this purpose, in this very study, the employment aluminium was not introduced yet very good gap profile and nanogap size was achieved by purely using chemical etching. The recipe for chemical etchant is (HCl 1:3 HN_3). A repeated resist trimming was introduced until has been developed until closed 50 nm was obtained as shown in Fig. 1a. The arrays of etched gap are show in Fig. 1b prior to the chemical etching. Approximately linear decrease in size is achieved with for both resist and material etching from the standpoint metal etching it is highly anticipated that high rate of reaction is always expected this because of loose electron bond associated with metal molecular bonding at etching step the electrode resistance and conductance are measured. The resistance and conductance profile for chemical etching shown in Fig. 3a and b. Figure 2 the final etch nanogap electrode profile produced by the chemical etching. As mentioned earlier, during and after the chemical etching the nano-gap electrode is covered by the photolithography based photoresist mask, this was done to prevent chemical from getting touch the wanted device part. Nanogap of 3 nm was successfully produced by this technique.

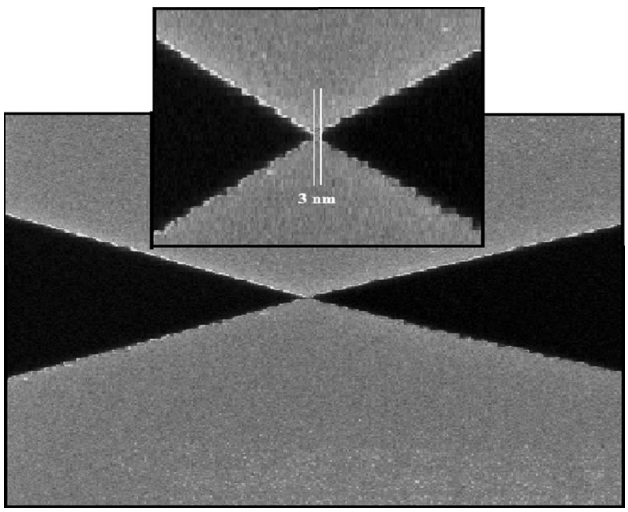

Fig. 2 FESEM images show 3 nm gold electrode pattern after using an aqua regia solution (HCl 1:3 HN_3) sequent to remove undesired gold material between the two electrodes

Figure 3 shown fabricated Nano gap conductance and resistance with Au configuration. Au gap behave much similar with semiconductor such as silicon at the nano domain and this is due to electro quantization as the device become smaller enhanced of its conductance The slightly differences in behavior of these three gap configuration, 15, 8 and 6 nΩ for 15, 5 and 3 nm respectively and how the resistance obtained with 15 nm is very high compared to other two gaps sizes and this due can be explained within the coulomb transport phenomena. By associating the separation gap for sole generation of resonances in the between the two electrode with a Coulomb charging energy. A suitable frequency of operation that is sufficiently low for complete gap operation can be established and metal resistivity is not stable with high frequency. Within the electrode, it would expect the conductance to be exponentially by increase a factor columbic distance, this can be seen in the Fig. 3b, with linear increase in conductance as gad size reduced. There are many reason for that, among them is ability of the electron to cross to the opposite electrode

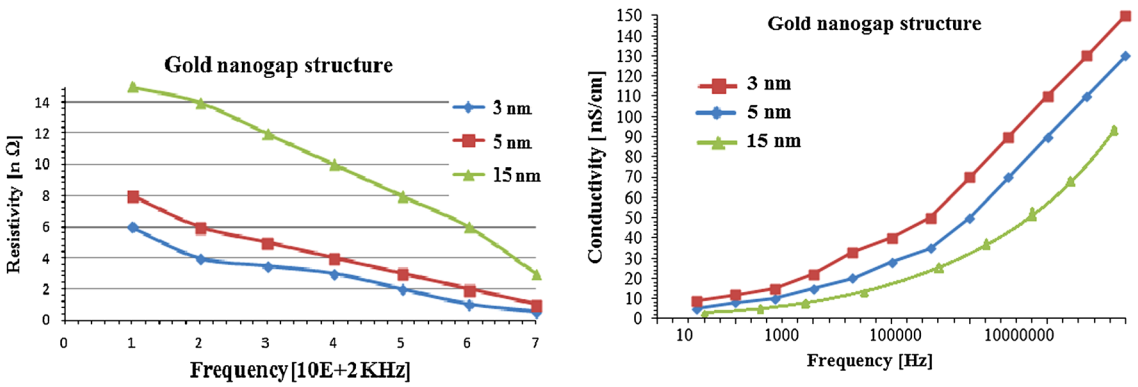

Fig. 3 Resistivity and conductivity parameters for the gold devices with different nanogaps size

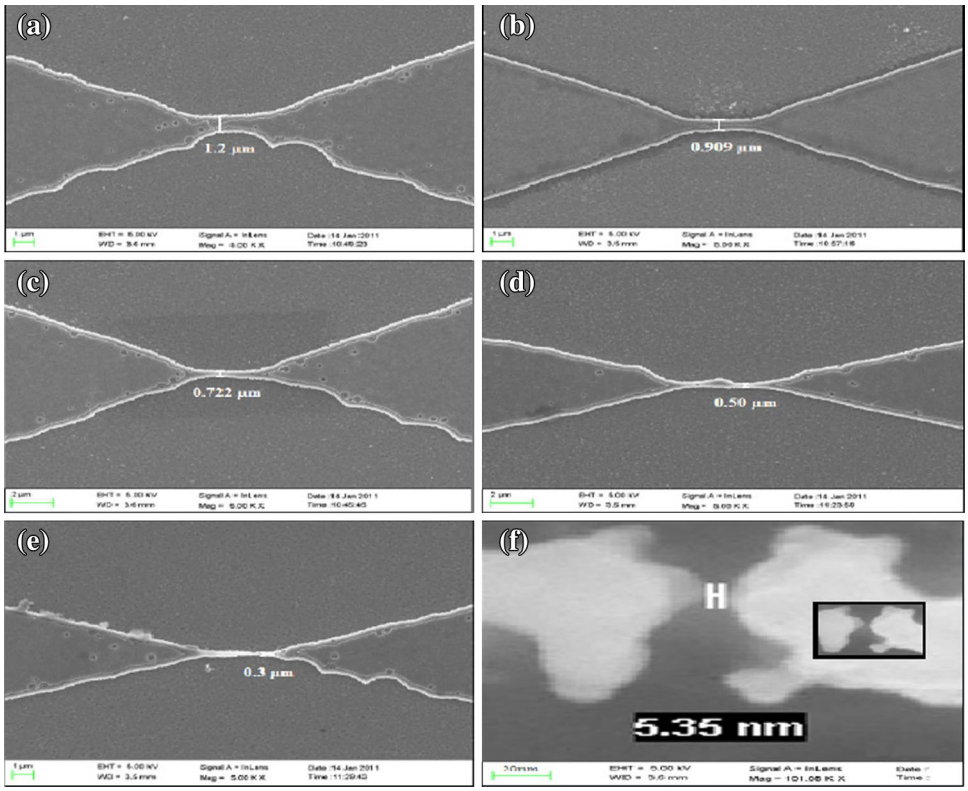

Fig. 4 FESEM images showing (**a**–**e**) the pattern thickness and **f** fabricated polysilicon nanogap, at the end of sequential oxidation and etching. The images are at the end of **a** 20 min **b** 40 min **c** 60 min **d** 70 min **e** 80 min, and **f** 90 min cyclic oxidation and BOE etching (Dhahi et al. 2012)

with minimum required energy and it can be concluded that, Au nanogap can be fabricated and be used much more better that using semiconductor materials and The three devices were tested for conductivity against the measured frequency response of nanogaps fabricated by the method described in the experiment section and more details can found in our previous publication. This approach enables down-scaling of the micro structure done to atomic sizes and will path way to 1-dimensions of experimental elements to explore electrochemistry in new regimes and to enhance sensitivity and selectivity. The proposed approach provide the opportunity to build arrays minutes size components with high controllability and repeatability.

Figure 4 show the fabricated poly-silicon nanogap, the device was fabricated by the method according and the phenomena behind the reaction between oxygen and silicon is diffusive (Dhahi et al. 2011, 2012; Adam and Hashim 2014) in nature and the phenomena of interaction atomic level between oxygen and silicon is also diffusion process as where the relatively open structure of silicon–oxygen molecules diffused through the growing SiO_2 (Dhahi et al. 2011, 2012; Adam and Hashim 2014). The oxidizing species are transported from the bulk gas to the gas/oxide interface with Flux. The species are transported across the growing oxide toward the poly-silicon surface with different Flux and react at the Si/SiO2 interface with another Flux. The decreasing profile of the gap was observed using FESEM, the characterization can found in (Dhahi et al. 2011, 2012). At each step of trimming process has been completed, the device current–voltage (I–V) characteristic is then measured by using a Keithley 4200 Semiconductor Parameter Analyser. During this process, a measurement process was set-up, a typical I–V measurement setting is employed on to the two terminal fabricated Nanogap devices by supplying voltages to the two electrode. From the Fig. 5, we can noticed that the gap behavior by observing the resistance and conductance changes as become smaller.

The Fig. 5, show the poly–silicon Nano gap electrical profile, gap resistance and gap conductance were observed as typical characteristics of a silicon gap behavior. The nanogap had gap size of sub −5 nm, as also confirmed in FESEM in Fig. 4. In this case, resistance was also observed; This characteristic is similar to electrical behavior characteristic of Au. However, is much more similar that of the silicon. The resistance become lower and conductance increase, this is due to the enhance electron mobility cause by nanogap electrode closing to each other (see Fig. 6).

The variation in electrical profiles for silicon nanogaps are shown in Fig. 7 above, clear discrepancies in resistance are indicate electro statistic agitation with respect to frequency changes, suggesting its intrinsic electron confinement is shown. 50 nΩ for 75 nm, 25 nΩ and with ~8 nΩ at low frequency are shown with different frequencies. Conductivity is the quality of a medium to respond to the changes in the electronic exchange and reorientation of the dipoles in response to the changing electric field. At low frequency, the scope for

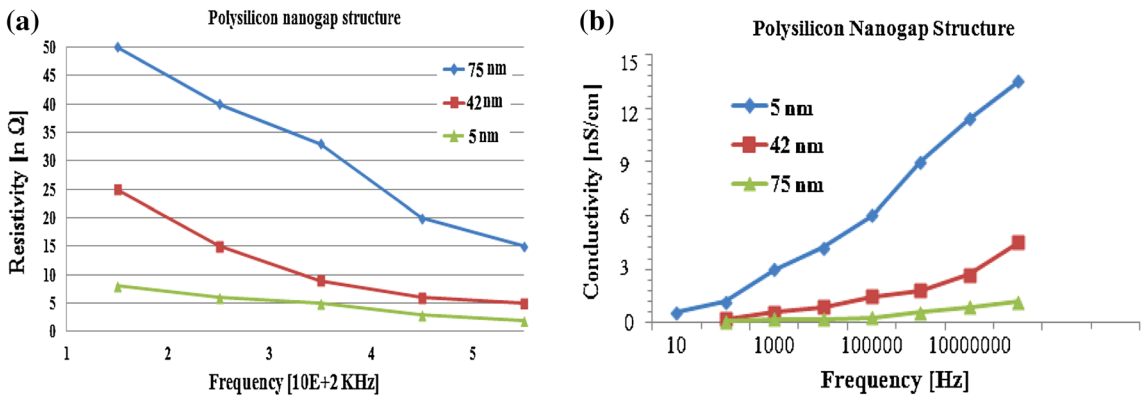

Fig. 5 **a** resistivity and **b** conductivity parameters for the devices with different nanogaps size

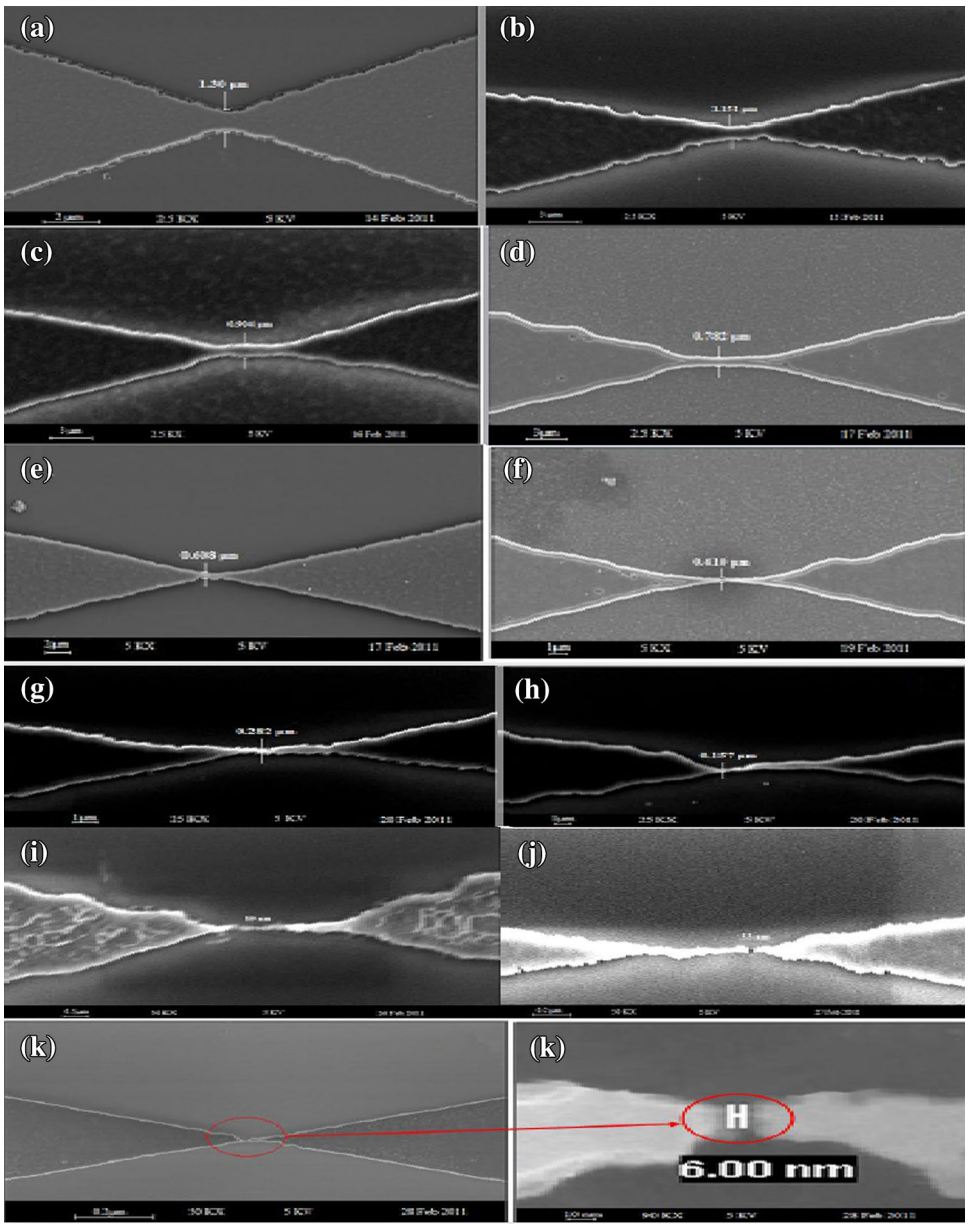

Fig. 6 The FESEM images of the silicon nanogap structure after etching with BOE solution at the end of each thermal oxidation step. Shown are the silicon layers after BOE etching at the end of the 1st to the 9th cycles with 20 min of oxidation (**a**–**i**) and the 9th cycle with 15 min (**j**) and 10 min (**k**) of thermal oxidation (Dhahi et al. 2011a)

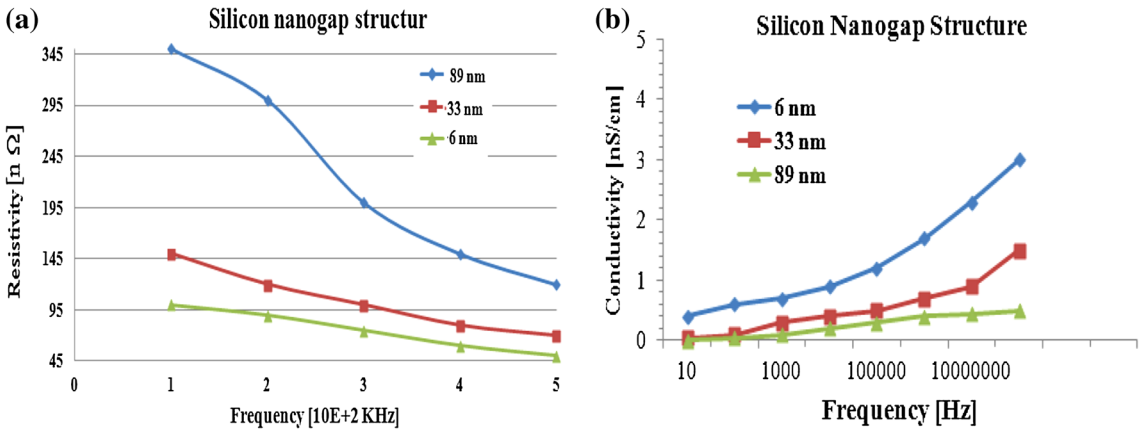

Fig. 7 Resistivity and conductivity parameters for the silicon devices with different nanogaps size

reorientation of the dipole is very high because of the huge interval time. At the higher frequency, the mean interval time is enough to allow a change in polarity and reorientation of the dipoles, producing stronger signals. Whereas, at high frequency the change in signal polarity is too short and therefore the dipoles cannot get enough time to reorient and respond to the changing field. Therefore, at high frequency the dipoles are too slow to respond to the changing electric field and thus the medium is insensitive to changes which were reflected in the form of low permittivity.

4 Conclusion

This paper present a novel fabrication methods to develop both metal and semiconductor nano-gap electrodes. Three configurations of nanogap electrodes were successfully fabricated with the size of less than 5 nm by using the conventional lithography process coupled with chemical and oxidation etching process. All the three material show similar electrical behavior with Au showing higher resistance stability in higher frequency domain, hence, with their novel electric potential and ease of fabrication; silicon, poly–silicon and Au nanogaps can be developed to become a portable novel and highly sensitive rapid detection device. The gap can be fabricated in such a way that can accommodated only single molecule and single-molecule measurements can provide information that is not achievable with traditional measurements system.

References

Adam T, Hashim U (2014) Highly sensitive silicon nanowire biosensor with novel liquid gate control for detection of specific single-stranded DNA molecules. Biosens Electron 67:656–661

Dhahi TS, Ali ME, Hashim U, Saif AA, Nazwa T (2011a) 5 nm gap via conventional photolithography and pattern-size reduction technique. Int J Phys Sci 6(15):3649–3656

Dhahi TS, Hashim U, Ahmed NM (2011b) Reactive ion etching (RIE) for micro and nanogap fabrication. J Basrah Res Sci 37(2):11–20

Dhahi TS, Hashim U, Ali ME, Ahmed NM (2012) Fabrication of 6 nm gap on silicon substrate for power saving appliances. Int J Phys Sci 7(16):2414–2421

Du D, Zou Z, Shin Y et al (2010) Sensitive immunosensor for cancer biomarker based on dual signal amplification strategy of graphene sheets and multienzyme functionalized carbon nanospheres. Anal Chem 82(7):2989–2995

Hashim U, Nazwa T, Dhahi TS, Saifullah A (2011) Polysilicon nanogap structure development using size expansion technique. Microelectron Int 28(3):24–30

Jemmy S, Rosemary LS, Scotts DC (2010) Fabrication of nano-gap electrodes and nano wires using an electrochemical and chemical etching technique. J Micromec Microengineering 10:1–7

Kang S, Nieuwenhuis AF, Mathwig K, Mampallil D, Lemay SG (2013) Electrochemical single-molecule detection in aqueous solution using self-aligned nanogap transducers. ACS Nano 7(12):10931–10937

Kim JH, Hanul M, Seunghyup Y, Choi YK (2012) Nanogap electrode fabrication for a nanoscale device by volume-expanding electrochemical synthesis. Small 1(2):1–7

Mampallil D, Mathwig K, Kang S, Lemay SG (2014) Reversible adsorption of outer-sphere redox molecules at Pt electrodes. J Phys Chem Lett 5(3):636–640

Singh KV, Bhura DK, Nandamuri G, Whited AM, Evans D, King J, Solanki R (2011) Nanoparticle-enhanced sensitivity of a nanogap-interdigitated electrode array impedimetric biosensor. Langmuir 27(22):13931–13939

Zanetti Ionescu C, Nevill JT, Di Carlo D, Jeong KH, Lee LP (2006) Nanogap capacitors: sensitivity to sample permittivity changes. J Appl Phys 99(2):024305

Zhong Z, Wu W, Wang D et al (2010) Nanogold-enwrapped graphene nanocomposites as trace labels for sensitivity enhancement of electrochemical immunosensors in clinical immunoassays: carcinoembryonic antigen as a model. Biosens Bioelectron 25(10):2379–2383